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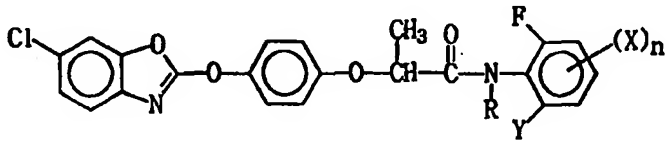

(1)

(57) Abstract

The present invention relates to novel herbicidal phenoxypropionic acid N-alkyl-N-2-fluorophenyl amides represented in formula (1), a method for preparing thereof, their use to control barnyard grass produced from rice and composition as suitable herbicides. In said formula, R is methyl or ethyl group; X is hydrogen, halogen, cyano, C_1~C_6 alkyl, C_1~C_6 alkoxy, C_1~C_3 haloalkyl substituted with 1 to 3 of halogen atom(s), C_1~C_3 haloalkoxy substituted with 1 to 3 of halogen atom(s), C_2~C_4 alkoxyalkoxy, phenoxy, benzyloxy, C_2~C_6 alkenyl, C_2~C_6 alkinyl, C_2~C_6 alkenyloxy, C_2~C_6 alkinyloxy, or phenyl group; Y is hydrogen or fluoro; n is an integer of 1 or 2 and when n is 2, X can be in a combination of other substituents.

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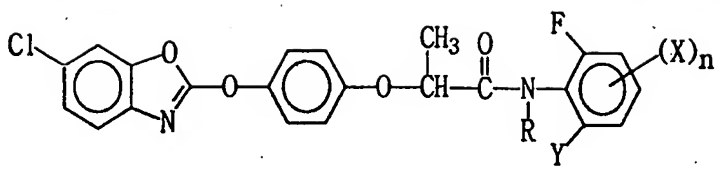
HERBICIDAL PHENOXYPROPIONIC ACID N-ALKYL-N-2-FLUORO PHENYL AMIDE COMPOUNDS

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to novel herbicidal phenoxypropionic acid N-alkyl-N-2-fluorophenyl amide compounds represented in the following formula (1), a method for preparing thereof, their use to control barnyard grass produced from rice and composition as suitable herbicides.



(1)

wherein,

R is methyl or ethyl group;

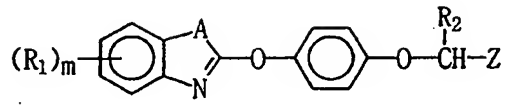
X is hydrogen, halogen, cyano, $C_1 \sim C_6$ alkyl, $C_1 \sim C_6$ alkoxy, $C_1 \sim C_3$ haloalkyl substituted with 1 to 3 of halogen atom(s), $C_1 \sim C_3$ haloalkoxy substituted with 1 to 3 of halogen atom(s), $C_2 \sim C_4$ alkoxyalkoxy, phenoxy, benzyloxy, $C_2 \sim C_6$ alkenyl, $C_2 \sim C_6$ alkinyl, $C_2 \sim C_6$ alkenyloxy, $C_2 \sim C_6$ alkinyloxy, or phenyl group;

Y is hydrogen or fluoro;

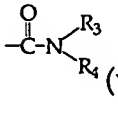
n is an integer of 1 or 2 and when n is 2, X can be in a combination of other substituents.

Description of the Prior Art

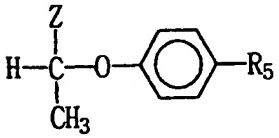
US Patent No. 4 130 413 discloses the compound containing the following formula (2).



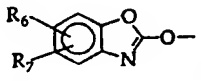
(2)

wherein, $(R_1)_m$ is hydrogen, halogen, CF_3, NO_2, CN or alkyl group; A is O, S or NH; R_2 is hydrogen or alkyl group; Z is  (where R_3 and R_4, that are the same or different, are hydrogen, $C_1 \sim C_6$ alkyl, $C_1 \sim C_6$ hydroxyalkyl, $C_3 \sim C_6$ cycloalkyl, $C_1 \sim C_4$ alkoxy, or phenyl substituted where 1 to 3 sbstituents are selected from $C_1 \sim C_4$ alkyl group, $C_1 \sim C_6$ alkoxy group, halogen and CF_3

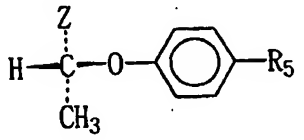
US Patent No. 4 531 969 discloses the compounds containing the following formula (3).



(3)

wherein, R_5 is  (where R_6 is hydrogen or halogen atom, R_7 is hydrogen or alkyl group); Z is the same as defined above.

US Patent No. 5 254 527 discloses the compounds containing the following formula (4).



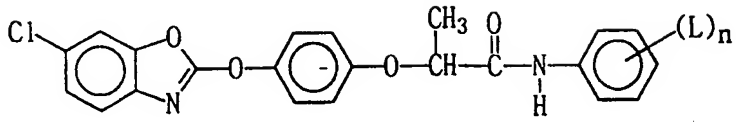
(4)

wherein, R_5 and Z are the same as defined above.

None of the patents teaches the synthesis of the compound represented in the above formula (1) and have tested the same for herbicidal activity.

JP Patent publication 2-11580 discloses the compound represented in the

following formula (5).



(5)

wherein, L is lower alkyl, halogen, methoxy, methoxyphenoxy, methylthio or methylvinyl group; n is an integer of 0 to 2.

JP Patent publication sho 53-40767 and sho 54-112828 also disclose that phenoxypropionic acid amide derivatives have herbicidal activity.

However, none of reports including the patents mentioned above has taught a method for preparing the compounds in the above formula (1) and tested the same against herbicidal activity. And also it has not been reported that the compounds have superior herbicidal activity and selectivity toward rice and control barnyard grass produced from rice.

SUMMARY OF THE INVENTION

Even though many of herbicides for rice have been recently developed and used, barnyard grass among weeds is the biggest problem in rice paddy.

Development of herbicides to control barnyard grass is an urgent to one who is in the field of agriculture. After transplanting young rice, herbicides, developed until now, cannot effectively control the production of barnyard grass so that it causes a huge damage to harvest. It has been reported that when barnyard grass is produced for one week in 1 m^2, amount of harvest decreases by 2%, for 5 weeks by about 10%, for 10 weeks by 19% and for 20 weeks by 35%.

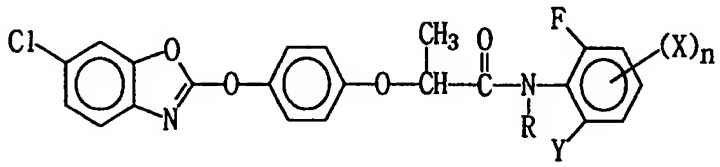
Many herbicides have been used for the purpose of controlling barnyard grass that damages in amount of harvest of rice. However, the herbicide with a broader herbicidal activity, environmentally-friendly property

and cost-effectiveness is still in demand.

The inventors have intensively studied to prepare herbicides to effectively control barnyard grass. As a result, they completed this invention to find a novel phenoxypropionic acid N-alkyl-N-2-fluorophenyl amide and its derivatives that are stable to rice and selectively control barnyard grass. This superior effectiveness is distinguished from the conventional inventions.

Detailed Description of the Invention

The present invention is characterized by novel phenoxypropionic acid N-alkyl-N-2-fluorophenyl amide represented in the following formula (1) with an excellent herbicidal activity as well as selectively stable toward rice.

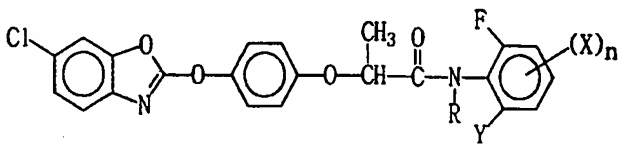


(1)

wherein, R, X, Y and n are the same as previously defined.

The compounds of the formula (1) according to the present invention may be specified as the following Table 1.

Table 1



(1)

R	Y	X
CH_3	H	H
CH_2CH_3	H	H
CH_3	H	4-CN
CH_3	H	4-F
CH_3	H	3-F
CH_3	H	5-F
CH_3	H	4-Cl
CH_3	H	4,5-F_2
CH_3	H	4-Br
CH_3	H	4-phenyl
CH_3	H	4-CH_3
CH_3	H	3-Br
CH_3	H	4-CH_2CH_3
CH_3	H	4-propyl
CH_3	H	4-isopropyl
CH_3	H	4-cyclopropyl
CH_3	H	4-butyl
CH_3	H	4-isobutyl
CH_3	H	3-CN
CH_3	H	4-OCH_3

(cont'd)

R	Y	X
CH_3	H	4-O-phenyl
CH_3	H	4-OEt
CH_3	H	4-O-isopropyl
CH_3	H	4-O-allyl
CH_3	H	4-O-propyl
CH_3	F	H
CH_3	F	3-F
CH_3	F	4-F
CH_2CH_3	F	4-F
CH_3	F	4-Cl
CH_3	F	4-Br
CH_3	F	4-CH_3
CH_3	F	4-CH_2CH_3
CH_3	F	4-propyl
CH_3	F	4-isopropyl
CH_3	F	4-cyclopropyl
CH_3	F	4-butyl
CH_3	F	4-isobutyl
CH_3	F	4-OCH_3
CH_3	F	4-OEt
CH_3	F	4-O-isopropyl
CH_3	F	4-O-propyl
CH_3	H	3,5-F_2

(cont'd)

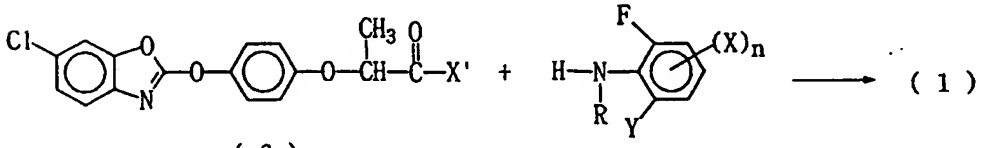
R	Y	X
CH_3	H	5-F
CH_3	H	5-Cl
CH_3	H	5-Br
CH_3	H	5-CN
CH_3	H	5-CH_3
CH_3	H	5-CH_2CH_3
CH_3	H	5-phenyl
CH_3	H	5-propyl
CH_3	H	5-isopropyl
CH_3	H	5-cyclopropyl
CH_3	H	5-butyl
CH_3	H	5-isobutyl
CH_3	H	5-OCH_3
CH_3	H	5-OEt
CH_3	H	5-O-isopropyl
CH_3	H	5-O-propyl
CH_3	H	5-O-phenyl
CH_3	H	5-O-allyl
CH_3	F	5-H
CH_3	F	5-F
CH_3	F	5-Cl
CH_3	F	5-Br
CH_3	F	5-CH_3

(cont'd)

R	Y	X
CH_3	F	5-CH_2CH_3
CH_3	F	5-propyl
CH_3	F	5-isopropyl
CH_3	F	5-cyclopropyl
CH_3	F	5-n-butyl
CH_3	F	5-isobutyl
CH_3	F	5-OCH_3
CH_3	F	5-OEt
CH_3	F	5-O-isopropyl
CH_3	F	5-O-propyl

The compounds of formula (1) according to this invention can be synthesized by a conventional method represented in the following scheme 1, reacting a compound of the formula (6) with a compound of the formula (7).

Scheme 1



(6) (7) (1)

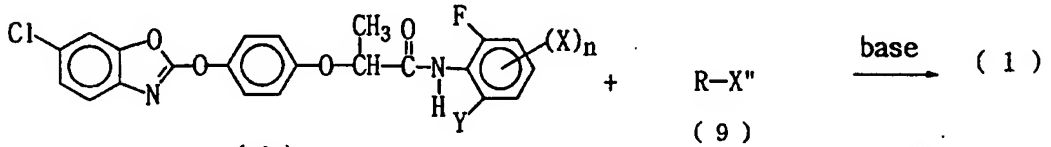
wherein, X' is OH, Cl, Br or phenoxy group; R, X, Y and n are the same as previously defined.

In the method according to scheme 1, it is prefer to use a binder such as triphenylphosphine and an organic base such as triethylamine or pyridine by keeping temperature at 0 ~ 100℃ in an inert solvent such as ethers like tetrahydrofuran, ethyethyl acetate, acetonitrile, toluene, xylene, hexane, methylene chloride, carbon tetrachloride, dichloroethane or the like, and to

purify the crude product by column chromatography.

Another method for preparing the compounds (1) represented in the following scheme 2 is an alkylation of a compound of the formula (8) to compounds of the formula (9).

Scheme 2



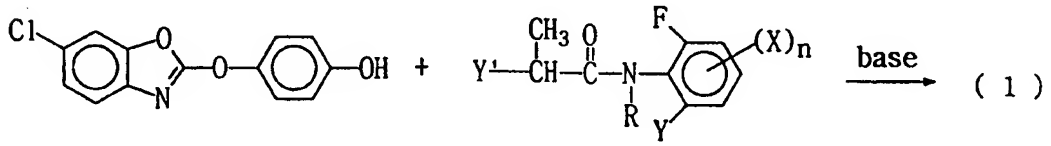
(8) (9)

wherein, X", which is a leaving group, is Cl, Br, I, benzenesulfonyloxy, toluenesulfonyloxy, methanesulfonyloxy or lower alkyl sulfate group; R, X, Y and n are the same as previously defined.

In scheme 2, it is prefer to use a strong base which is enough to pull out a hydrogen from amide, NH. The strong base used in this invention is NaOH, KOH, LiOH, NaH, n-BuLi or LDA. It is prefer to carry this reaction at the temperature of -78 ~ 50℃ in an inert solvent such as ethers like ethylether, dioxane or tetrahydrofuran or hydrocarbons like hexane.

Another method for preparing the compounds (1) represented in the following scheme 3 is a reaction of a compound of the formula (10) with a compound of the formula (11) in the presence of a base.

Scheme 3



(10) (11)

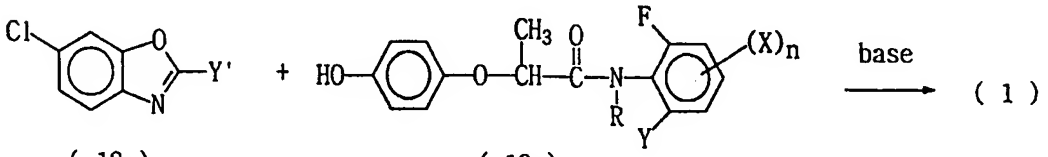
wherein, Y' is halogen, alkylsulfonyloxy, haloalkylsulfonyloxy, benzenesulfonyloxy or toluenesulfonyloxy group; R, X, Y, and n are the same as previously defined.

In Scheme 3, it is prefer to use inorganic bases such as alkali metal hydroxides like sodium hydroxide or potassium hydroxide, alkali metal carbonates like sodium carbonate or potassium carbonate, alkali metal hydrogencarbonates like sodium hydrogencarbonate or potassium hydrogencarbonate or organic bases like triethylamine, N,N-dimethylaniline, pyridine or 1,8-diazabicyclo[5,4,0]undec-7-ene.

A phase transition catalyst such as tetra-*n*-butylammonium bromide or 18-crown-6-[1,4,7,10,13,16-hexaoctacyclooctadecane] can be added to complete a reaction rapidly, if necessary. And also one or more than two solvents can be combined and used, if deemed necessary. It is prefer to use an inert organic solvent; for example; ketones such as acetone; aromatic hydrocarbons such as toluene, xylene or chlorobenzene; aliphatic hydrocarbons such as petroleum ether or ligroin; ethers such as diethylether, tetrahydrofuran or dioxane; nitriles such as acetonitrile or propionitrile; or amides such as N,N-dimethylformamide, N,N-dimethylacetamide, N-methylpyrrolidone. A reaction is carried at the temperature of from 0℃ to reflux, preferably 5 ~ 50℃ for 1 to 24 hour(s) to afford a high yield.

Another method for preparing the compound (1) represented in the following scheme 4 is a reaction of a compound of the formula (12) with a compound of the formula (13) in the presence of a base.

Scheme 4



(12) (13)

wherein, X, Y, Y', R and n are the same as previously defined.

In Scheme 4, it is prefer to use inorganic bases; for example; alkali metal hydroxides such as sodium hydroxide or potassium hydroxide, alkali metal carbonates such as sodium carbonate or potassium carbonate, alkali metal hydrogencarbonates such as sodium hydrogencarbonate or potassium hydrogencarbonate or organic bases such as triethylamine, N,N-dimethylaniline, pyridine, picoline, quinoline, or 1,8-diazabicyclo[5,4,0]undec-7-ene.

A phase transition catalyst such as tetra-*n*-butylammonium bromide or 18-crown-6[1,4,7,10,13,16-hexaoctacyclooctadecane] can be used, if necessary. And also one or more than two solvents can be combined and used if deemed necessary. It is prefer to use an inert organic solvent; for example; ketones such as acetone or butanone; aromatic hydrocarbons such as benzene, toluene, xylene or chlorobenzene; aliphatic hydrocarbons such as petroleum ether, or ligroin; ethers such as diethylether, tetrahydrofuran or dioxane; nitriles such as acetonitrile or propionitrile; or amides such as N,N-dimethylformamide, N,N-dimethyl acetamide or N-methylpyrrolidone. A reaction is carried at the temperature of from 0℃ to reflux, preferably 20 ~ 100℃ for 1 to 24 hour(s) to afford a high yield.

The present invention is explained in more detail by the following examples but is not limited by these examples.

Example 1: N-(2-fluorophenyl)-N-methyl-2-bromo-propionamide

2-Bromopropionic acid(3.4 g, 0.022 mol) and 2-fluoroaniline(3 g, 0.024 mol) were dissolved in 50 ㎖ of chloroform and cooled to 0℃. A solution of dicyclohexylcarbodiimide(5 g, 0.024 mol) in 10 ㎖ of chloroform was slowly injected through a syringe. A temperature of the reaction mixture was raised to room temperature and it was stirred for 1 hour. Solid remained during the reaction was filtered out and washed twice with 20 ㎖ of chloroform. The

filtrate was concentrated under reduced pressure and the crude product was purified by column chromatography (eluent; ethyl acetate/n-hexane = 1/3) to afford 5 g of the target product.

^{1}H-NMR($CDCl_3$) : δ 1.7(3H, d), 3.24(3H, s), 4.16(0.7H, q), 4.34(0.3H, q), 7.13~7.48(4H, m)

Example 2:N-(2-fluorophenyl)-N-methyl-2-(4-hydroxyphenoxy)propionamide

N-(2-fluorophenyl)-N-methyl-2-bromo-propionamide(18.2 g, 0.07 mol), hydroquinone(7 g, 0.064 mol), potassium carbonate(10.54 g, 0.076 mol) and tetra-*n*-butylammonium bromide(1 g) were dissolved in 350 ㎖ of acetonitrile and heated at reflux for 6 hours. The reaction mixture was cooled to room temperature and solid remained during the reaction was filtered out. The filtrate was concentrated under reduced pressure and the crude product was purified by column chromatography(eluent: ethyl acetate/n-hexane = 1/2) to afford 16 g of the target product.

^{1}H-NMR($CDCl_3$) : δ 1.42(3H, t), 3.25(3H, s), 4.56(1H, q), 6.5~7.4(8H, m)

Example 3 : 2-[4-(6-chloro-2-benzoxazoyloxy)-phenoxy]propionic acid-N-(2-fluorophenyl)-N-methylamide

N-(2-fluorophenyl)-N-methyl-2-(4-hydroxyphenoxy)propionamide (11.5 g, 0.04 mol), 2,6-dichlorobenzoxazole (6.85 g, 0.036 mol), potassium carbonate (6 g, 0.043 mol) and tetra-*n*-butylammonium bromide (1 g) were dissolved in 300 ㎖ of acetonitrile and heated at reflux for 7 hours. The reaction mixture was cooled to room temperature and solid remained during the reaction was filtered out. The filtrate was concentrated under reduced pressure and the crude product was purified by column chromatography (eluent: ethyl acetate/n-hexane = 1/3) to afford 12.5 g of the target product.

^{1}H-NMR($CDCl_3$) : δ 1.42(3H, t), 3.3(3H, s), 4.62(1H, m), 6.8~7.4(11H, m)

Example 4 : 2-[4-(6-chloro-2-benzoxazoyloxy)-phenoxy]propionic acid-N-(2-fluorophenyl)amide

2-[4-(6-chloro-2-benzoxazoyloxy)-phenoxy]propionic acid (346.7 ㎎, 1 mmol) was dissolved in 10 ㎖ of tetrahydrofuran. 2-fluoroaniline(111.12 ㎎, 1 mmol), triphenylphosphine(393.4 ㎎, 1.5 mmol), triethylamine(0.15 ㎖, 1 mmol) and carbon tetrachloride(1 ㎖) were added sequentially and heated at reflux for 8 hours. The reaction mixture was cooled to room temperature and acidified with 5% hydrochloric acid, followed by addition of water. The acidified reaction mixture was extracted three times with ethyl acetate. The combined organic solvent layer was dried over magnesium sulfate, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography(eluent: ethyl acetate/n-hexane = 1/4) to afford 200 ㎎ of the target product.

m.p : 132 ~ 136℃

^{1}H-NMR($CDCl_3$) : δ 1.7(3H, d), 4.81(1H, q), 7.05~7.45(10H, m), 8.35(1H, m), 8.5(1H, br)

Example 5 : 2-[4-(6-chloro-2-benzoxazoyloxy)-phenoxy]propionic acid-N-(2-fluorophenyl)-N-methyl amide

2-[4-(6-chloro-2-benzoxazoyloxy)-phenoxy]propionic acid-N-(2-fluorophenyl)amide (100 ㎎, 0.24 mmol) was dissolved in 10 ㎖ of anhydrous tetrahydrofuran and 60% NaH(10 ㎎, 0.24 mmol) and CH_3I(34 ㎎, 0.24 mmol) were added sequentially at 0℃. The reaction mixture was stirred at room temperature for 5 hours. Ice water was poured to the reaction mixture and it was extracted three times with ethyl acetate. The combined organic solvent layer was dried over magnesium sulfate, filtered and concentrated under reduced pressure. The crude product was purified by column

chromatography(eluent: ethyl acetate/n-hexane = 1/4) to afford 75 ㎎ of the target product.

^{1}H-NMR($CDCl_3$) : δ 1.42(3H, t), 3.3(3H, s), 4.62(1H, m), 6.8~7.4(11H, m).

Example 6 : 2-[4-(6-chloro-2-benzoxazoyloxy)-phenoxy]propionic acid-N-(2-fluorophenyl)-N-methyl amide

2-[4-(6-chloro-2-benzoxazoyloxy)-phenoxy]propionic acid(346.7 ㎎, 1 mmol) was dissolved in 10 ㎖ of tetrahydrofuran and N-methyl-2-fluoroaniline(125 ㎎, 1 mmol), triphenylphosphine(393.4 ㎎, 1.5 mmol), triethylamine(0.15 ㎖, 1 mmol) and carbon tetrachloride(1 ㎖) were added sequentially and the reaction was heated at reflux for 12 hours. The reaction mixture was cooled to room temperature and acidified with 5% hydrochloric acid, followed by addition of water. The acidified reaction mixture was extracted three times with ethyl acetate. The combined organic solvent layer was dried over magnesium sulfate, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography(eluent: ethyl acetate/n-hexane = 1/2) to afford 100 ㎎ of the target product.

Example 7 : 2-[4-(6-chloro-2-benzoxazoyloxy-phenoxy)propionic acid-N-ethyl-N-(2-fluorophenyl)amide

2-[4-(6-chloro-2-benzoxazoyloxy)-phenoxy]-N-(2-fluorophenyl)propionamide(100 ㎎, 0.24 mmol) was dissolved in 10 ㎖의 anhydrous tetrahydrofuran and 60% NaH(10 ㎎, 0.24 mmol) and bromoethane(27 ㎎, 0.24 mmol) were added sequentially at 0℃ and then the reaction mixture was stirred at room temperature for 8 hours. Ice water was poured to the reaction mixture and it was extracted three times with ethyl acetate. The combined organic solvent layer was dried over magnesium sulfate, filtered and concentrated under

reduced pressure. The crude product was purified by column chromatography(eluent: ethyl acetate/n-hexane = 1/2) to afford 60 ㎎ of the target product.

^{1}H-NMR($CDCl_3$) : δ 1.1(3H, t), 1.42(3H, d), 3.8(2H, q), 4.62(1H, q), 6.7~7.4(11H, m)

Example 8 : 2-[4-(6-chloro-2-benzoxazoyloxy)-phenoxy]propionic acid-N-methyl-N-(2,4,5-trifluoro phenyl)amide

2-[4-(6-chloro-2-benzoxazoyloxy)-phenoxy]propionic acid(0.693 g, 2 mmol) was dissolved in 15 ㎖ of tetrahydrofuran and N-methyl-2,4,5-trifluoroaniline(0.322g, 2 mmol), triphenylphosphine(0.78g, 2 mmol), triethylamine(0.4 ㎖) and carbon tetrachloride(2 ㎖) were added sequentially and then the reaction mixture was heated at reflux for 18 hours. The reaction mixture was cooled to room temperature and acidified with 5% hydrochloric acid. The acidified reaction mixture was extracted three times with ethyl acetate. The combined organic solvent layer was dried over magnesium sulfate, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography(eluent: ethyl acetate/n-hexane = 1/2) to afford 250 ㎎ of the target product.

^{1}H-NMR($CDCl_3$) : δ 1.42(3H, d), 3.2(3H, s), 4.65(1H, m), 6.6~7.4(9H, m)

Example 9 : 2-[4-(6-chloro-2-benzoxazoyloxy)-phenoxy]propionic acid-N-methyl-N-(2,6-difluoro-phenyl)amide

2-[4-(6-chloro-2-benzoxazoyloxy)-phenoxy]propionic acid(0.693 g, 2 mmol) and N-methyl-2,6-difluoroaniline(0.284 g, 2 mmol) were dissolved in 20 ㎖ of tetrahydrofuran and triphenylphosphine(0.78 g, 2 mmol), triethylamine(0.42 ㎖) and carbon tetrachloride(2 ㎖) were added sequentially. The reaction mixture was heated at reflux for 16 hours. The reaction mixture

was cooled to room temperature and acidified with 5% hydrochloric acid. The acidified reaction mixture was extracted three times with ethyl acetate. The combined organic solvent layer was dried over magnesium sulfate, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography(eluent: ethyl acetate/n-hexane = 1/2) to afford 205 ㎎ of the target product.

^{1}H-NMR($CDCl_3$) : δ 1.4(3H, d), 3.3(3H, s), 4.62(1H, q), 6.8~7.4(10H, m)

Example 10 : 2-[4-(6-chloro-2-benzoxazoyloxy)-phenoxy]propionic acid-N-(2,4-difluorophenyl)-N-methyl amide

2-[4-(6-chloro-2-benzoxazoyloxy)-phenoxy]propionic acid(0.693 g, 2 mmol) was dissolved in 15 ㎖ of tetrahydrofuran and N-methyl-2,4-difluoroaniline(0.284 g, 2 mmol), triphenylphosphine(0.78 g, 2 mmol), triethylamine(0.42 ㎖) and carbon tetrachloride(2 ㎖) were added sequentially. The reaction mixture was heated at reflux for 16 hours. The reaction mixture was cooled to room temperature and acidified with 5% hydrochloric acid, followed by addition of water. The acidified reaction mixture was extracted three times with ethyl acetate. The combined organic solvent layer was dried over magnesium sulfate, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography(eluent: ethyl acetate/n-hexane = 1/2) to afford 230 ㎎ of the target product.

^{1}H-NMR($CDCl_3$) : δ 1.4(3H, d), 3.2(3H, s), 4.6(1H, q), 6.6~7.2(10H, m)

Example 11 : 2-[4-(6-chloro-2-benzoxazoyloxy)-phenoxy]propionic acid-N-methyl-N-(2,3,6-trifluorophenyl)amide

2-[4-(6-chloro-2-benzoxazoyloxy)-phenoxy]propionic acid(0.693g, 2 mmol) was added to 6 ㎖ of thionyl chloride and the reaction mixture was

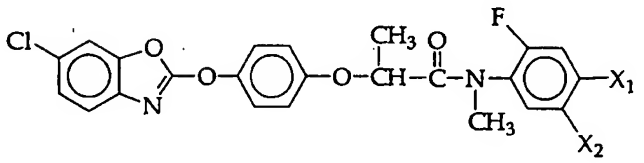
heated at reflux for 2 hours. Excess of thionyl chloride was removed under reduced pressure and 3 ㎖ of anhydrous tetrahydrofuran was added to it. A solution of N-methyl-2,3,6-trifluoroaniline(0.32 g, 2 mmol) and triethyl amine(0.42 ㎖) in anhydrous tetrahydrofuran(10 ㎖) was added slowly to the reaction mixture at 0℃. The mixture was stirred at 0℃ for 30 minutes and stirred at room temperature for additional 1 hour. After pouring water the reaction mixture was extracted three times with ethyl acetate. The combined organic solvent layer was dried over magnesium sulfate, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography(eluent: ethyl acetate/n-hexane = 1/2) to afford 240 ㎎ of the target product.

^{1}H-NMR($CDCl_3$) : δ 1.45(3H, d), 3.25(3H, s), 4.6(1H, q), 6.7~7.4(9H, m)

Example 12 ~ 17

The compounds represented in the following Table 2 were prepared by the same procedure of example 11 except using of aniline compounds instead of N-methyl-2,3,6-trifluoroaniline.

Table 2



Example	X_1	X_2	^{1}H-NMR($CDCl_3$)
Exam. 12	H	CH_3	1.42(3H, t), 2.3(3H, s), 3.25(3H, s), 4.62(1H, m), 6.8~7.4(10H, m)
Exam. 13	Cl	H	1.42(3H, t), 3.3(3H, s), 4.62(1H, m), 6.7~7.5(10H, m)
Exam. 14	H	F	1.42(3H, t), 3.3(3H, s), 4.62(1H, m), 6.5~7.4(10H, m)
Exam. 15	CH_3	H	1.42(3H, t), 2.38(3H, s), 3.25(3H, s), 4.62(1H, m), 6.8~7.4(10H, m)
Exam. 16	OCH_3	H	1.42(3H, t), 3.25(3H, s), 3.8(3H, s), 4.65(1H, m), 6.65~7.45(10H, m)
Exam. 17	OCH_2CH_3	H	1.25(3H, t), 1.42(3H, t), 3.25(3H, s), 4.0(2H, q), 4.62(1H, m), 6.65~7.42(10H, m)

Formulation

In order to use the compounds according to the present invention as herbicides, they should be formulated in such a suitable type such as wettable powder, emulsions, granules, dusts, suspensions and solutions by combining a carrier, a surfactant, a dispersing agent or a supplement agent. Many of these may be applied directly or after diluted with suitable media. Formulations can be prepared at spray volume of from hundreds liters to thousands liters per hectare. The formulations contain about 0.1% to 99% by weight of active ingredient(s) and 0.1% to 20% surfactant(s) or 0% to 99.9% solid or liquid

diluent(s) are recommended to be added. The formulations will contain these ingredients in the following approximate proportions shown in Table 3.

Table 3

Formulations	Weight Percent(%)		
	Active ingredient	Diluent	Surfactant
Wettable powders	10 ~ 90	0 ~ 74	1 ~ 10
Suspension	3 ~ 50	40 ~ 95	0 ~ 15
Emulsions· Solution	3 ~ 50	40 ~ 95	0 ~ 15
Granules	0.1 ~ 95	5 ~ 99.9	1 ~ 15

The proportion of active ingredients is depending on the intended use. Higher ratios of a surfactant to active ingredients are sometimes desirable and are achieved by incorporation into the formulation or tank mixing.

Solid diluents with high absorption are preferred for wettable powders. Liquid diluents and solvents are preferably stable against phase separation at 0℃. All the formulations may contain a small amount of additives to prevent forming, caking, corrosion and growth of microorganisms.

According to conventional methods to prepare the composition, solutions can be made only by blending ingredients and fine solids by blending and pulverizing with hammer-mill . Suspensions can be made by wet-milling and granules can be made by spraying the active ingredients on performed granular carrier.

Preparation examples of typical formulations are as follows.

Formulation 1 : Wettable powders

The ingredients are thoroughly blended, re-blended after spraying

liquid surfactant on the solid ingredients and hammer-milled until all the solids are essentially under 100㎛.

Active ingredient(Example 3 Compound)	20 wt%
Dodecylphenol polyethylene glycol ether	2 wt%
Sodium ligninsulfonate	4 wt%
Sodium silicon aluminate	6 wt%
Montmorillonite	68 wt%

Formulation 2 : Wettable powders

The ingredients are blended, hammer-milled until all the solids are under 25㎛ and packaged.

Active ingredient(Example 3 Compound)	80 wt%
Sodium alkyl naphthalenesulfonate	2 wt%
Sodium ligninsulfonate	2 wt%
synthetic amorphous silica	3 wt%
Kaolinite	13 wt%

Formulation 3 : Emulsions

The ingredients are mixed and homogeneously dissolved to give emulsions.

Active ingredient(Example 3 Compound)	30 wt%
Cyclohexanone	20 wt%
Polyoxyethylene alkylaryl ether	11 wt%
Calcium alkylbenzenesulfonate	4 wt%
Methylnaphthalene	35 wt%

Formulation 4 : Granules

The ingredients were thoroughly blended. 20 Weight part of water was

added to 100 weight part of the ingredient mixture. The ingredient mixture was granulated with a size of 14 to 32 mesh by using extrusive granulator and dried.

Active ingredient(Example 3 Compound)	5 wt%
Sodium laurylalcoholsulfonate	2 wt%
Sodium ligninsulfonate	5 wt%
Carboxymethyl cellulose	2 wt%
Potassium sulfate	16 wt%
Plaster	70 wt%

The formulations according to this invention were sprayed with diluting to a certain concentration.

Utility

The compounds according to the present invention represent high activity as leaf treatment herbicides for rice and especially effective in rice due to an excellent control of barnyard grass.

The active ingredients can be used from 10 g to 4 kg per hectare, preferably from 50 g to 400 g. The amount of the compounds of the present invention depends on the amount and size of weeds and formulations. The herbicides of the present invention can be used as alone or in combination with other herbicides, insecticides or bactericides. Especially it is essential to add one or more of agents selected from the group consisting of bentazon, Quinclorac, propanil, simetryn, 2,4-D, fenoxaprop-ethyl, linuron, MCPA, azafenidin, carfentrazone, molinate, thiobencarb, pendimethalin, bensulfuron-methyl, pyrazosulfuron-ethyl, metsulfuron-methyl, thifensulfuron-methyl, tribenuron-methyl, trifluralin, amidosulfuron, bromoxynil, butachlor, mecoprop, metribuzin, bifenox, benfuresate, isoproturon, cyhalofop-butyl, mefenaset, fentrazamide, pyriminobac-methyl, bispyribac sodium, azimsulfruon, cyclosulfamuron and pyanchor.

The herbicidal effect of the compounds of this invention was tested and the examples are as follows.

Experimental example 1 : Leaf treatment test

Seeds of rice, wheat, barley, corn, cotton, barnyard grass, common sorgum, large crabgrass and fall panicum were seeded at a pot with a surface area of 600 ㎠. When barnyard grass kept at 20 ~ 30℃ had three leaves, wettable powders prepared by mixing 1 weight part of the active compound, 5 weight part of acetone and 1 weight part of emulsifier and diluted with water was applied directly on the leaves in 2000 ℓ per hectare. The concentration of the spray liquid was so chosen the particular amounts of the active compound desired. 14 days after the treatment, the degree of damage to the plants was rated in % damage in comparison to the development of untreated control.

0% no action (like untreated control)

20% slight effect

70% herbicidal effect

100% total destruction

In the test, the active compound(s) of the formula (1) according to the invention exhibited an excellent selectivity toward the plants and herbicidal activity against weeds.

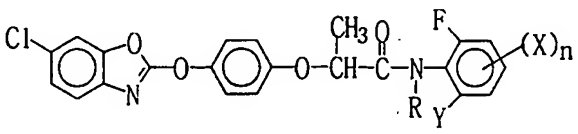
The plants employed in this test are as follows.

Table 4

ABRV.	SCIENTIFIC NAME	ENGLISH NAME
ZEAMX	*Zea mays* L.	Corn
GLXMA	*Glycine max*(L.) MERR	Soy bean
GOSHI	*Gossypium*	Cotton
TRZAW	*Triticum aestivum* L.	Wheat
ORYSA	*Oryza sativa L.* cv. Dongjin	Rice
SORBI	*Andropogon sorghum*	Common sorgum
ECHCG	*Echinochloa crus-galli* Beauv. var. *caudata* Kitagawa	Barnyard grass
DIGSA	*Digitaria Sanguinalis* (L.) SCOP	Large crabgrass
PANDI	*Panicum dichotomiflorum* Michx	Fall panicum

Among the compounds of the formula (1), herbicidal activity of the compounds in table 5 is represented in the following table 6 and 7.

Table 5



(1)

Compound No.	R	Y	X
1	CH_3	H	H
2	CH_2CH_3	H	H
3	CH_3	H	4,5-F_2
4	CH_3	F	H
5	CH_3	H	4-F
6	CH_3	F	3-F
7	CH_3	H	5-CH_3
8	CH_3	H	4-Cl
9	CH_3	H	5-F
10	CH_3	H	4-CH_3
11	CH_3	H	4-OCH_3
12	CH_3	H	4-OCH_2CH_3
control 1	H	H	H
control 2 (Fenoxaprop-ethyl)			

Table 6

Active Compound	Weeds	Treated amount (kg/ha)		
		0.4	0.1	0.025
Compound No.1	ZEAMX	100	70	0
	GLXMA	20	0	0
	GOSHI	0	0	0
	TRZAW	0	0	0
	ORYSA	0	0	0
	SORBI	100	100	100
	ECHCG	100	100	90
	DIGSA	100	100	100
	PANDI	100	100	100
Compound No.2	ZEAMX	70	10	5
	GLXMA	10	0	0
	GOSHI	0	0	0
	TRZAW	0	0	0
	ORYSA	0	0	0
	SORBI	100	95	40
	ECHCG	95	80	20
	DIGSA	100	95	30
	PANDI	100	100	0
Compound No.3	ZEAMX	0	0	0
	GLXMA	10	0	0
	GOSHI	0	0	0
	TRZAW	0	0	0
	ORYSA	10	0	0
	SORBI	100	100	40
	ECHCG	95	60	0
	DIGSA	100	90	30
	PANDI	0	0	0

(cont'd)

Active Compound	Weeds	Treated amount (kg/ha)		
		0.4	0.1	0.025
Compound No.4	ZEAMX	100	40	10
	GLXMA	20	0	0
	GOSHI	0	0	0
	TRZAW	0	0	0
	ORYSA	30	20	0
	SORBI	100	100	95
	ECHCG	100	95	80
	DIGSA	100	100	90
	PANDI	100	100	40
Compound No.5	ZEAMX	100	30	0
	GLXMA	0	0	0
	GOSHI	0	0	0
	TRZAW	0	0	0
	ORYSA	0	0	0
	SORBI	100	100	100
	ECHCG	100	100	0
	DIGSA	100	100	100
	PANDI	100	80	40
Compound No.6	ZEAMX	100	100	30
	GLXMA	0	0	0
	GOSHI	0	0	0
	TRZAW	0	0	0
	ORYSA	20	0	0
	SORBI	100	100	100
	ECHCG	100	100	95
	DIGSA	100	100	40
	PANDI	100	100	40

(cont'd)

Active Compound	Weeds	Treated amount (kg/ha)		
		0.1	0.05	0.025
Compound No.7	ZEAMX	0	0	0
	GLXMA	10	0	0
	GOSHI	0	0	0
	TRZAW	0	0	0
	ORYSA	0	0	0
	SORBI	100	95	10
	ECHCG	40	40	20
	DIGSA	100	100	100
	PANDI	100	100	100
Compound No.8	ZEAMX	0	0	0
	GLXMA	0	0	0
	GOSHI	0	0	0
	TRZAW	0	0	0
	ORYSA	0	0	0
	SORBI	100	70	0
	ECHCG	70	0	0
	DIGSA	100	95	30
	PANDI	100	0	0
Compound No.9	ZEAMX	100	0	0
	GLXMA	0	0	0
	GOSHI	0	0	0
	TRZAW	0	0	0
	ORYSA	20	0	0
	SORBI	100	100	90
	ECHCG	80	80	70
	DIGSA	100	100	100
	PANDI	100	100	90

(cont'd)

Active Compound	Weeds	Treated amount (kg/ha)		
		0.1	0.05	0.025
Compound No.10	ZEAMX	0	0	0
	GLXMA	0	0	0
	GOSHI	0	0	0
	TRZAW	0	0	0
	ORYSA	0	0	0
	SORBI	100	60	30
	ECHCG	80	0	0
	DIGSA	100	95	70
	PANDI	70	0	0
Compound No.11	ZEAMX	0	0	0
	GLXMA	0	0	0
	GOSHI	0	0	0
	TRZAW	0	0	0
	ORYSA	0	0	0
	SORBI	70	20	0
	ECHCG	40	0	0
	DIGSA	95	95	95
	PANDI	40	20	-
Compound No.12	ZEAMX	0	0	0
	GLXMA	0	0	0
	GOSHI	0	0	0
	TRZAW	0	0	0
	ORYSA	00	0	0
	SORBI	30	0	0
	ECHCG	30	0	0
	DIGSA	100	100	80
	PANDI	0	0	0

(cont'd)

Active Compound	Weeds	Treated amount (kg/ha)		
		0.4	0.1	0.025
control 1	ZEAMX	100	100	100
	GLXMA	40	30	0
	GOSHI	0	0	0
	TRZAW	30	20	0
	ORYSA	70	50	35
	SORBI	100	100	100
	ECHCG	100	100	100
	DIGSA	100	100	100
	PANDI	100	100	100
control 2	ZEAMX	100	100	80
	GLXMA	30	0	0
	GOSHI	0	0	0
	TRZAW	70	60	0
	ORYSA	90	70	40
	SORBI	100	100	100
	ECHCG	100	100	100
	DIGSA	100	100	100
	PANDI	100	100	95

Table 7

Active Compound	4 Leaves	Treated amount (kg/ha)			
		1.0	0.25	0.063	0.016
Compound No.1	rice	0	0	0	0
	Barnyard grass	100	100	100	75
control 2	rice	85	70	30	20
	Barnyard grass	100	100	100	95

Experimental example 2 :

Rice[*Oryza sativa. L. cv.* Chuchong(ORYSA)] and barnyard grass [*Echinocgloa crus-galli* beauv. var. *caudate* Kitagawa(ECHCG) and *Echinocgloa crus-galli* Beauv. var. *orygicola* Ohwi (ECHOR)] were planted and grown. The test compounds with 98% purity was dissolved in acetone containing tween-20 and diluted with water. Each maximum concentration of acetone and tween-20 were 25% and 0.1%.

The solution was sprayed in a proportion of 200 g a.i per hactare on the leaves. When rice(ORYSA) had 6.0 ~ 6.5 leaves with 32.8 ㎝ of the first leaf, barnyard grass(ECHOR) had 1 ~ 2 tillering with 37.3 ㎝ of the first leaf and barnyard grass(ECHCG) had 1 ~ 2 tillering with 44.4 ㎝ of the first leaf.

20 and 30 days after treatment (DAT) herbicidal effect and toxicity were measured. The result is represented in the following table 8.

Table 8

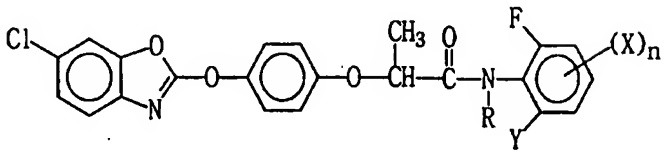
Active Compound	Formulation	Amount (%)	Treated amount	activity(0~100), 20DAT		toxicity(0~100)	
				ECHOR	ECHCG	20DAT	30DAT
Compound	Tech.	98%	200	100	99.5	0	0
control 1	Tech.	98%	200	100	100	22	39

As a result of these tests, the compounds of the present invention exhibit an excellent selectivity toward rice and herbicidal activity against barnyard grass. And also it is proved that the compounds are very stable for the plants and useful to control weeds.

CLAIMS

What is claimed is :

1. A herbicidal compound of the formula (1).



(1)

wherein,

R is methyl group or ethyl group;

X is hydrogen, halogen, cyano, $C_1 \sim C_6$ alkyl, $C_1 \sim C_6$ alkoxy, $C_1 \sim C_3$ haloalkyl substituted with 1 to 3 of halogen atom(s), $C_1 \sim C_3$ haloalkoxy substituted with 1 to 3 of halogen atom(s), $C_2 \sim C_4$ alkoxyalkoxy, phenoxy, benzyloxy, $C_2 \sim C_6$ alkenyl, $C_2 \sim C_6$ alkinyl, $C_2 \sim C_6$ alkenyloxy, $C_2 \sim C_6$ alkinyloxy, or phenyl group;

Y is hydrogen or fluoro;

n is an integer of 1 or 2, when n is 2, X can be in a combination of other substituents.

2. The herbicidal compound as defined in claim 1, wherein said R is CH_3; X is H, F, Cl, Br, CN, CH_3 or OCH_3; said Y is H, or F ; said n is 1.

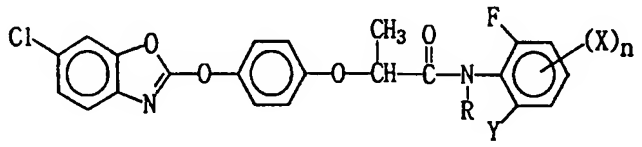
3. The herbicidal compound as defined in claim 1, wherein said R is CH_3; said X is H ; said Y is H.

4. The herbicidal compound as defined in claim 1, wherein said R is CH_3; said X is 5-CH_3; said Y is H.

5. The herbicidal compound as defined in claim 1, wherein said R is CH_3;

said X is 4,5-F_2 ; said Y is H.

6. A method to control barnyard grass produced from growing rice without any harm by applying the compounds of the formula (1) with effective amount.



(1)

wherein,

R is methyl group or ethyl group;

X is hydrogen, halogen, cyano, C_1~C_6 alkyl, C_1~C_6 alkoxy, C_1~C_3 haloalkyl substituted with 1 to 3 of halogen atom(s), C_1~C_3 haloalkoxy substituted with 1 to 3 of halogen atom(s), C_2~C_4 alkoxyalkoxy, phenoxy, benzyloxy, C_2~C_6 alkenyl, C_2~C_6 alkinyl, C_2~C_6 alkenyloxy, C_2~C_6 alkinyloxy, or phenyl group;

Y is hydrogen or fluoro;

n is an integer of 1 or 2, when n is 2, X can be in a combination of other substituents.

7. The method to control barnyard grass as defined in claim 6, wherein said compound of the formula (1) is that R is CH_3; X는 H, F, Cl, Br, CN, CH_3 or OCH_3; Y is H or F; n is 1.

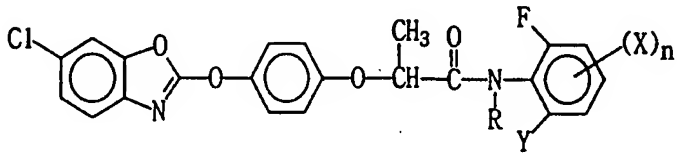
8. The method to control barnyard grass as defined in claim 6, wherein said compound of the formula (1) is that R is CH_3; X is H; Y is H.

9. The method to control barnyard grass as defined in claim 6, wherein

said compound of the formula (1) is that R is CH_3; X is 5-CH_3; Y is H.

10. The method to control barnyard grass as defined in claim 6, wherein said compound of the formula (1) is that R is CH_3; X is 4,5-F_2; Y is H.

11. The herbicidal composition comprising the compound of the formula (1) and agriculturally acceptable carrier, supplement agent, surfactant or other herbicidal compounds.



(1)

wherein,

R is methyl or ethyl group;

X is hydrogen, halogen, cyano, $C_1 \sim C_6$ alkyl, $C_1 \sim C_6$ alkoxy, $C_1 \sim C_3$ haloalkyl substituted with 1 to 3 of halogen atom(s), $C_1 \sim C_3$ haloalkoxy substituted with 1 to 3 of halogen atom(s), $C_2 \sim C_4$ alkoxyalkoxy, phenoxy, benzyloxy, $C_2 \sim C_6$ alkenyl, $C_2 \sim C_6$ alkinyl, $C_2 \sim C_6$ alkenyloxy, $C_2 \sim C_6$ alkinyloxy, or phenyl group;

Y is hydrogen or fluoro;

n is an integer of 1 or 2, when n is 2, X can be in a combination of other substituents.

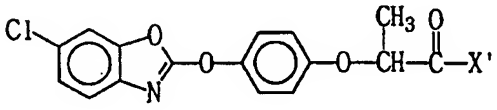
12. The herbicidal composition as defined in claim 11, wherein said compound of formula (1) is that R is CH_3; X is H, F, Cl, Br, CN, CH_3 or OCH_3; Y is H or F; n is 1.

13. The herbicidal composition as defined in claim 11, wherein said compound of formula (1) is that R is CH_3; X is H; Y is H.

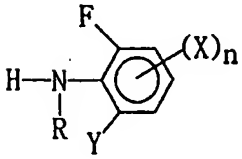
14. The herbicidal composition as defined in claim 11, wherein said compound of formula (1) is that R is CH_3; X is 5-CH_3; Y is H.

15. The herbicidal composition as defined in claim 11, wherein said compound of formula (1) is that R is CH_3; X is 4,5-F_2; Y is H.

16. A method for preparing the compound (1) by reacting the compound of the formula (6) and the compound of the formula (7).



(6)



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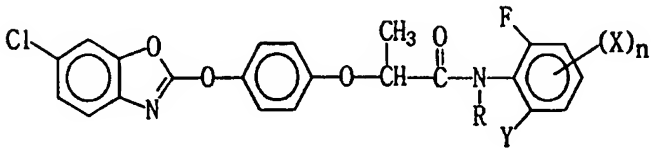


(1)

wherein,

R is methyl or ethyl group;

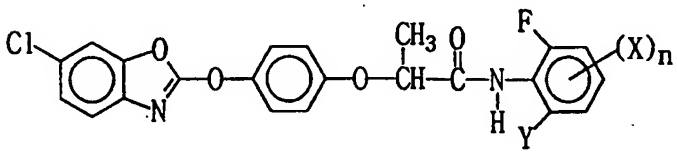
X is hydrogen, halogen, cyano, $C_1 \sim C_6$ alkyl, $C_1 \sim C_6$ alkoxy, $C_1 \sim C_3$ haloalkyl substituted with 1 to 3 of halogen atom(s), $C_1 \sim C_3$ haloalkoxy substituted with 1 to 3 of halogen atom(s), $C_2 \sim C_4$ alkoxyalkoxy, phenoxy, benzyloxy, $C_2 \sim C_6$ alkenyl, $C_2 \sim C_6$ alkinyl, $C_2 \sim C_6$ alkenyloxy, $C_2 \sim C_6$ alkinyloxy, or phenyl group;

Y is hydrogen or fluoro;

n is an integer of 1 or 2, when n is 2, X can be in a combination of other substituents; and

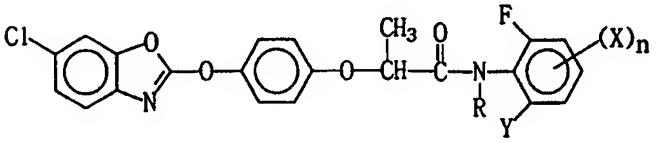
X' is OH, Cl, Br or phenoxy group.

17. A method for preparing the compound (1) by reacting the compound of the formula (8) and the compound of the formula (9).



(8)

R—X" (9)



(1)

wherein,

R is methyl or ethyl group;

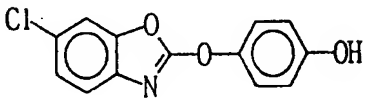
X is hydrogen, halogen, cyano, $C_1 \sim C_6$ alkyl, $C_1 \sim C_6$ alkoxy, $C_1 \sim C_3$ haloalkyl substituted with 1 to 3 of halogen atom(s), $C_1 \sim C_3$ haloalkoxy substituted with 1 to 3 of halogen atom(s), $C_2 \sim C_4$ alkoxyalkoxy, phenoxy, benzyloxy, $C_2 \sim C_6$ alkenyl, $C_2 \sim C_6$ alkinyl, $C_2 \sim C_6$ alkenyloxy, $C_2 \sim C_6$ alkinyloxy, or phenyl group;

Y is hydrogen or fluoro;

n is an integer of 1 or 2, when n is 2, X can be in a combination of other substituents; and

X" is Cl, Br, I, benzenesulfonyloxy, toluenesulfonyloxy, methanesulfonyloxy or lower alkyl sulfate group.

18. A method for preparing the compound (1) by reacting the compound of the formula (10) and the compound of the formula (11).



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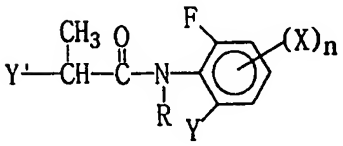
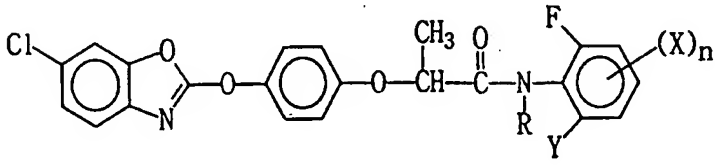


(11)



(1)

wherein,

R is methyl or ethyl group;

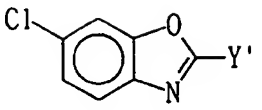
X is hydrogen, halogen, cyano, $C_1 \sim C_6$ alkyl, $C_1 \sim C_6$ alkoxy, $C_1 \sim C_3$ haloalkyl substituted with 1 to 3 of halogen atom(s), $C_1 \sim C_3$ haloalkoxy substituted with 1 to 3 of halogen atom(s), $C_2 \sim C_4$ alkoxyalkoxy, phenoxy, benzyloxy, $C_2 \sim C_6$ alkenyl, $C_2 \sim C_6$ alkinyl, $C_2 \sim C_6$ alkenyloxy, $C_2 \sim C_6$ alkinyloxy, or phenyl group;

Y is hydrogen or fluoro;

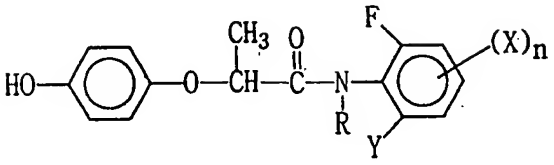
n is an integer of 1 or 2, when n is 2, X can be in a combination of other substituents; and

Y' is halogen, alkylsulfonyloxy, haloalkylsulfonyloxy, benzenesulfonyloxy or toluenesulfonyloxy group.

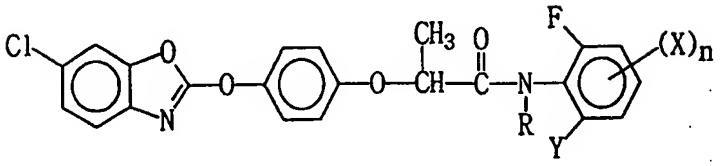
19. A method for preparing the compound (1) by reacting the compound of the formula (12) and the compound of the formula (13).



(12)



(13)



(1)

wherein,

R is methyl or ethyl group;

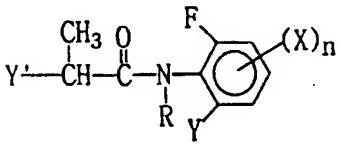
X is hydrogen, halogen, cyano, $C_1 \sim C_6$ alkyl, $C_1 \sim C_6$ alkoxy, $C_1 \sim C_3$ haloalkyl substituted with 1 to 3 of halogen atom(s), $C_1 \sim C_3$ haloalkoxy substituted with 1 to 3 of halogen atom(s), $C_2 \sim C_4$ alkoxyalkoxy, phenoxy, benzyloxy, $C_2 \sim C_6$ alkenyl, $C_2 \sim C_6$ alkinyl, $C_2 \sim C_6$ alkenyloxy, $C_2 \sim C_6$ alkinyloxy, or phenyl group;

Y is hydrogen or fluoro;

n is an integer of 1 or 2, when n is 2, X can be in a combination of other substituents; and

Y' is halogen, alkylsulfonyloxy, haloalkylsulfonyloxy, benzenesulfonyloxy or toluenesulfonyloxy group.

20. An intermediate compound of formula (11).



(11)

wherein,

R is methyl or ethyl group;

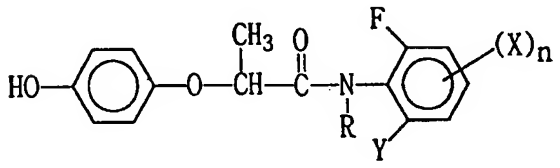
X is hydrogen, halogen, cyano, $C_1 \sim C_6$ alkyl, $C_1 \sim C_6$ alkoxy, $C_1 \sim C_3$ haloalkyl substituted with 1 to 3 of halogen atom(s), $C_1 \sim C_3$ haloalkoxy substituted with 1 to 3 of halogen atom(s), $C_2 \sim C_4$ alkoxyalkoxy, phenoxy, benzyloxy, $C_2 \sim C_6$ alkenyl, $C_2 \sim C_6$ alkinyl, $C_2 \sim C_6$ alkenyloxy, $C_2 \sim C_6$ alkinyloxy, or phenyl group;

Y is hydrogen or fluoro;

n is an integer of 1 or 2, when n is 2, X can be in a combination of other substituents; and

Y' is halogen, alkylsulfonyloxy group, haloalkylsulfonyloxy group, benzenesulfonyloxy group, or toluenesulfonyloxy group.

21. An intermediate compound of formula (13).



(13)

wherein,

R is methyl or ethyl group;

X is hydrogen, halogen, cyano, $C_1 \sim C_6$ alkyl, $C_1 \sim C_6$ alkoxy, $C_1 \sim C_3$ haloalkyl substituted with 1 to 3 of halogen atom(s), $C_1 \sim C_3$ haloalkoxy substituted with 1 to 3 of halogen atom(s), $C_2 \sim C_4$ alkoxyalkoxy, phenoxy, benzyloxy, $C_2 \sim C_6$ alkenyl, $C_2 \sim C_6$ alkinyl, $C_2 \sim C_6$ alkenyloxy, $C_2 \sim C_6$ alkinyloxy, or phenyl group;

Y is hydrogen or fluoro;

n is an integer of 1 or 2, when n is 2, X can be in a combination of other substituents.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR 99/00401

A. CLASSIFICATION OF SUBJECT MATTER

IPC[7]: A 01 N 43/76; C 07 D 263/58; C 07 C 233/07, 309/04, 309/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC[7]: A 01 N; C 07 C; C 07 D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 02-011580 A (KUMIAI CHEM IND CO LTD) 16 January 1990 (16.01.90) PATENT ABSTRACT OF JAPAN, vol. 14, No. 137 (C-702), 15 March 1990 (15.03.90), abstract. (Cited in the application).	1-16,18,20
A	US 4130413 A (HANDTE ET AL.) 19 December 1978 (19.12.78) abstract, claims. (Cited in the application).	1-16
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A	US 5254527 A (NESTLER AT AL.) 19 October 1993 (19.10.93) claims. (Cited in the application).	1-16
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☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
„A" document defining the general state of the art which is not considered to be of particular relevance
„E" earlier application or patent but published on or after the international filing date
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„T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
„X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
„Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
„&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
24 November 1999 (24.11.99)	06 December 1999 (06.12.99)

Name and mailing adress of the ISA/AT	Authorized officer
Austrian Patent Office Kohlmarkt 8-10; A-1014 Vienna Facsimile No. 1/53424/200	Schnass Telephone No. 1/53424/217

Form PCT/ISA/210 (second sheet) (July 1998)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/KR 99/00401

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/KR 99/00401

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			PL	A1	212111	11-02-1980
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